Electroanalytical method development for the stripping voltammetric determination of metal ions with bismuth film modified electrodes

THESIS

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1. Introduction

One of the biggest challenges of today's analytical chemistry is the determination of metal ions in environmental and biological samples at lower and lower concentration level. In contrast to the analytical techniques such as atomic spectroscopy or ICP-OES, stripping analysis techniques are especially suitable for trace metal analysis due to their cheapness and simplicity. The extreme sensitivity of the stripping voltammetric method can be attributed to the combination of the efficient preconcentration of the analytes on a permanent surface electrode under controlled conditions and the oxidation or reduction of the accumulated components with a modern electroanalytical method or a chemical reaction. Beside sensitivity, the further advantage of the stripping voltammetric techniques is the opportunity to measure metal speciation, namely the free- and the complexed forms of the metal ions of the samples. Stripping analysis techniques significantly developed in the last 15 years. Beside the classic anodic stripping voltammetry, used for the determination of metals forming amalgam with mercury, adsorptive stripping voltammetry has also appeared and the application of modified electrodes has widely spread.

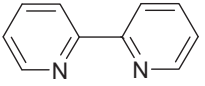
2. Aims

My PhD research is connected with both the anodic- and the adsorptive stripping metal analysis. My aim was to develop bismuth film electrode base electroanalytical methods which are suitable for sensitive and selective metal ion detection with the application of different organic complexing ligands and eliminate mercury as a significant environmentally pollutant electrode material. With the elaboration of the new electrode modification and voltammetric measurement method, my further aim was to improve the main analytical performance parameters – detection limit and selectivity – compared to the other stripping voltammetric techniques performed with similar chemically modified electrodes. Bismuth film electrode, as one of the possible alternatives of mercury film electrodes, was written and applied to stripping analysis in 2000. The number of the related publications has been increasing and the stripping voltammetric application of the bismuth film electrodes has become one of the most intensive research fields of electroanalytical chemistry.

3. Experimental part

3.1. Anodic stripping voltammetric method development

The aim of the anodic stripping voltammetric experiments was to deposit bismuth film on the surface of a glassy carbon electrode, modified previously with Nafion polymer film containing complexing ligands (2,2'-bipyridyl), to achieve lower detection limit compared to the similar methods published before.



Chemical structure of 2,2'-bipyridyl.

The main steps of the method in case of Pb^{2+} determination:

$$Pb^{2+}{}_{surf} / [PbL^{2+}]_{surf} + Bi^{3+}{}_{surf} + 5e^- \rightarrow Pb^{0}{}_{surf} + Bi^{0}{}_{surf} + L_{surf}$$

$$Pb^{0}{}_{surf} + Bi^{0}{}_{surf} \rightarrow Pb^{2+}{}_{aq} + Bi^{3+}{}_{aq} + 5e^-$$

L: 2,2'-bipyridyl

Acetic acid/sodium acetate buffer (0.1 M, pH 4.5) was used as voltammetric background electrolyte, and bismuth film was always deposited in situ, namely the bismuth ions were always reduced together with the analyte metal ions (Zn2+, Cd2+, Pb2+) onto the glassy carbon electrode surface. In the course of the anodic stripping voltammetric measurements, the target metal ions were reduced (accumulated) at -1,4 V (*vs.* Ag/AgCl/KCl) by using constant solution stirring. After a 5 s quiet time period, Osteryoung square wave voltammetry was applied to oxidize the metals reduced previously (stripping step). To take the advantage of the bismuth film, the dissolved oxygen has not been removed from the sample solution.

During the method development, the most important measurement parameters were optimized (the thickness and the ligand concentration of the electrode modification polymer layer, the thickness of the bismuth film, the quality and the pH value of the voltammetric solution, the deposition potential, the stirring rate, the accumulation time, and the voltammetric techniques used in the stripping step, and the parameters of the Osteryoung square wave voltammetry e.g. frequency, step potential, potential amplitude).

Due to the application of a polymer layer, an electrode regeneration step was necessary to work out for providing the suitable reproducibility of the method. The modified electrodes were regenerated in 0,1 M HCl solution for 5 min at constant solution stirring and then the electrodes were conditioned in 0,1 M NaCl /0,05 M potassium-hydrogen-phthalate buffer (pH 4.00) for 5 min. Later the whole regeneration process was performed in one step in a 0.1 M Na2EDTA solution for 1-2 min.

After the optimization of both the electrode modification and the voltammetric measurement parameters, the sensitivity of differently modified glassy carbon electrodes was compared at constant analyte concentration. Nafion/bismuth film, bismuth film, Nafion-bipyridyl-bismuth film, Nafion-bipyridyl, and Nafion modified glassy carbon electrodes were tested and the results approved that my proposed electrode modification (Nafion-2,2'-bipyridyl-bismuth film) provided the highest voltammetric sensitivity for all three metal ions. Therefore, the immobilization of the complexing ligands in a thin polymer layer is able to significantly increase the sensitivity of the anodic stripping voltammetric method.

The selectivity experiments proved that the anodic stripping voltammetric responses were not disturbed by the presence of the NH_4^+, Li^+, Na^+, K^+, Cs^+, Rb^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ag^+, Mn^{2+} and Ce^{4+} ions, however 10-fold excess of certain ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+} and Hg^{2+}) significantly disturbed the detection of the target metal ions.

As a last step of the anodic stripping voltammetric method development, calibration plots were recorded by using the previously optimized measurement parameters. The detection limits (LOD) obtained (0,37 nM Pb^{2+}, 1,1 nM Cd^{2+} and 8,6 nM Zn^{2+}) are related to the results measured in trace analysis, and the analytical performance of the proposed anodic stripping voltammetric method, performed with Nafion-2,2'-bipyridyl-bismuth film modified electrode, reaches or exceeds the performance of the methods using hanging mercury drop, mercury film or similarly prepared bismuth film electrodes.

Finally the method was applied to the analysis of metal ions in several real samples (white wine, Jodaqua natural water and tap water). Well defined stripping peaks were obtained for Zn^{2+} ions in tap water and Jodaqua water, while the concentration of Pb^{2+} and Cd^{2+} ions were below the limit of detection of the method, and Pb^{2+} concentration of the white wine sample was succeeded to measure. Each result was confirmed by an independent technique, ICP-MS.

3.2. Adsorptive stripping voltammetric method development

In case of adsorptive stripping voltammetry, the accumulation of the target metal ions is based on a selective chemical interaction. The target metal ions, complexed with different selective organic ligands, are usually accumulated by adsorption onto the electrode surface, and then the quantitative stripping response is obtained by reducing the metal ions from its complexed form. To improve the sensitivity of the method, bismuth film, deposited in *ex situ* way, is also used for these stripping methods, however, the stability and the reproducibility of the method is not suitable because bismuth film can easily oxidize in the air while the electrode is transferred from the bismuth film depositing solution to the sample solution.

For adsorptive stripping voltammetric measurements, the selective ligands have been used in polymer films, carbon paste and with immobilization to the electrode surface by adsorption, and none of these techniques take the advantages of bismuth film.

By considering these facts, the aim of the adsorptive stripping voltammetric measurements was to develop a new, fast, reproducable and sensitive bismuth film based method to the determination of lead ions at glassy carbon electrode modified with Nafion polymer containg calix[4]arene (T-3990) type ligand.

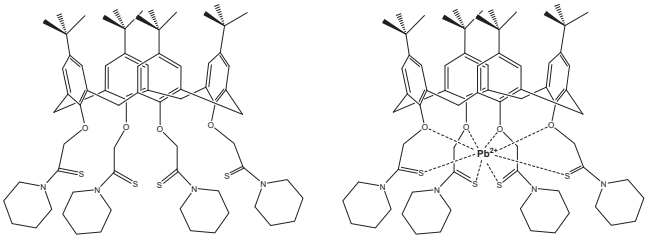
The proposed adsorptive stripping voltammetric method consists of two steps. During the first step, the modified electrode is held in the stirred sample solution (0,1 M acetic acid/sodium acetate, pH=1,0) for 10 min at open circuit to perform the complexation between the target ions and the selective ligand. Following the accumulation step, the electrode was transferred into the background electrolyte (0,1 M acetic acid/sodium acetate buffer, pH 4,5) containing bismuth ions (1 $mgdm^{-3}$) as well. The concentration of the complexed metal ions is measured parallel with *in situ* bismuth film deposition. Between the consecutive measurements, the modified electrode was regenerated in 0,1 M EDTA solution for 1-2 min.

<u>The main steps of the measurement:</u>

Accumulation at open circut: $Pb^{2+}_{aq} + L_{surf} \rightarrow [PbL^{2+}]_{surf}$, ahol L: T-3990 ionofor

Reduction: $[PbL^{2+}]_{surf} + Bi^{3+} + 5e^{-} \rightarrow Pb^{0}_{surf} + Bi^{0}_{surf} + L_{surf}$

Oxidation (stripping): $Pb^{0}_{surf} + Bi^{0}_{surf} \rightarrow Pb^{2+}_{aq} + Bi^{3+}_{aq} + 5e^{-}$



Chemical structure of T-3990 calixarene ligand and its lead ion complex.

During the optimization of the electrode modification, the optimal thickness and ligand concentration of the Nafion film was determined and then the adsorptive stripping voltammetric responses of differently modified glassy carbon electrodes. (Nafion/T-3990/bismuth film, Nafion/T-3990 and Nafion/bismuth film modified glassy carbon electrode) were compared at the same measurement conditions. The results obtained proved that the deposition of bismuth film significantly increased the sensitivity of the Nafion/T-3990 modified electrode.

Following the accumulation of the target metal ions at open circuit, the reduction and the oxidation (stripping) of the complexed ions was performed in the background electrolyte, separately from the sample solution by applying the measurement parameters optimized at the anodic stripping voltammetric method. After the optimization of the thickness of the bismuth film and the other parameters influencing the accumulation of the target ions (e.g. accumulation time, the quality of the sample solution) , calibration plot was recorded. The detection limit of the method (LOD) was calculated on the basis of three times of the means (n=10) of the background noise and it was found 0,1 nM after 10 min preconcentration time. The reproducibility of the analytical signals was characterized by a relative standard deviation value at 41 μg/L Pb^{2+} concentration which was 1,12%.

Beside sensitivity, selectivity is undoubtedly the most important advantage of the adsorptive stripping voltammetric method, because in case of the anodic stripping voltammetry, different interfering ions of the sample solution are reduced simultaneous with the target ions making the detection impossible. The selectivity experiments proved that those ions (Cu^{2+} Zn^{2+} Cd^{2+}) which have significant influence on the voltammetric detection of lead, do not disturb the adsorptive stripping voltammetric detection of Pb^{2+} at its 100-fold excess. These experiments were repeated in the presence of 1000-fold excess

of different ions (Cu^{2+} Zn^{2+} Cd^{2+}, Mn^{2+} Cu^{2+} NH_4^+ Fe^{2+}, Na^+ K^+ Ca^{2+} Mg^{2+}), and the stripping peak heights were compared with the ones obtained in background electrolyte containing only Pb^{2+} ions (relative signals). The results showed that the decrease of the stripping peak heights of lead was only approx. 20%, thus the voltammetric determination of Pb^{2+} ions can be carried out in such complexed sample solutions.

Finally, environmental water samples (tap- and rain water) were investigated with the elaborated adsorptive stripping voltammetric method.

4. Thesis

I. The *anodic stripping voltammetric* experiments firstly proved that, the application of the new type of electrode modification – modification of glassy carbon electrode with a polymer film which contains a selective organic complexing ligand and with an *in situ* plated bismuth film – significantly increased the sensitivity of the simultaneous determination of Zn^{2+}, Cd^{2+} and Pb^{2+} ions.

II. The *adsorptive stripping voltammetric* experiments firstly proved that, the application of the new bismuth film deposition technique – *in situ* bismuth film deposition in a background electrolyte after the accumulation at open circuit at a glassy carbon electrode modified with a polymer film which contains a calix[4]arene type selective organic ionophore – provided the opportunity for the selective, high sensitive determination of Pb^{2+} ions in such complexed samples where the anodic stripping method cannot be applied due to the distorting stripping voltammetric signals.

III. During both the *anodic and the adsorptive stripping voltammetric* methods it was proved that, the thickness of the polymer film on the electrode surface significantly influenced the voltammetric determination of the metal ions. The stripping voltammetric responses of metal ions *vs*. the polymer thickness function had a maximum point, and the scanning electron microscope studies proved that the thick films cracked and the target ions could escape through these openings into the bulk of the sample solution decreasing the sensitivity of the analysis.

IV. During both the *anodic and the adsorptive stripping voltammetric* methods it was proved that, the organic ligand concentration of the film significantly influenced the voltammetric responses of the metal ions. Scanning electron microscopy studies proved that, the high ligand concentration of the polymer film changed the adhesion properties of the film onto the electrode surface. Due to the increased amount of metal ion complex, the film partly peels off from the electrode surface decreasing the sensitivity of the analysis.

V. During both the *anodic and the adsorptive stripping voltammetric* methods it was proved that, the increase of the bismuth film thickness significantly improved the sensitivity of the voltammetric method.

VI. The application of a polymer film for both the *anodic and the adsorptive stripping voltammetric* methods, required the use of an electrode regeneration step due to the so called „memory effect". The experiments proved that, the regeneration, performed in a 0,1 M EDTA solution, was suitable for achieving the required reproducibility.

VII. During the optimization of the *anodic stripping voltammetric* method, it was proved that, the use of Osteryoung square wave voltammetry for the oxidation of the previously reduced metal ions provided the most sensitive stripping signals. By investigating the parameters of this voltammetric potential function it was found that the increase of the potential step, the square wave frequency and the potential amplitude, the voltammetric responses also increased, however, the voltammograms became distorted after reaching a maximum value.

VIII. The applicability of both the *anodic and the adsorptive stripping voltammetric* methods was tested and proved through the analysis of metal ions in real samples, and the results were confirmed with ICP-MS technique.

5. Publication list

Publications related to the thesis

F. Torma, M. Kadar, K. Toth, E. Tatar: Nafion/2,2'-bipyridyl-modified bismuth film electrode for anodic stripping voltammetry, Analytica Chimica Acta, *619*, **2008**, 173-182. (IF: 3,17)

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Tóth K., Gyurcsányi E.R., Torma F., Kádár M. Mészáros T.: Szintetikus receptor-alapú kémiai szenzorok: fejlesztési irányok és az érzékelők néhány élelmiszeranalitikai alkalmazása. MTA Tudományos Kollokvium – Központi Élelmiszertudományi Kutatóintézet. Magyarország, Budapest, **2010**. szeptember 24.

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